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The Thermodynamic State of the Deuterium-Palladium System

Gibbs Free Energy & Chemical Potential

Technical Note TN-7.1

by

J. L. Waisman & R. H. Summerl

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(The equilibrium diagram shows D+ Concentrations for any given
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The Thermodynamic State of the D-Pd System
Gibbs Free Energy & Chemical Potential

by

J. L. Waisman & R. H. Summerl

Abstract

To generate X-heat[1] in a D-Pd system, (1) a certain thermodynamic state of the deuterium dissolved in the palladium host must be produced and (2) the palladiium host must have appropriate crystal characteristics.[Ref1]

In this paper, the thermodynamic characteristics are presented; (1) the sequential thermodynamic processes (and their accompanying changes in free energy) necessary to enable a fusion reaction are summarized; (2) the derivation of the Gibbs free energy functions are reviewed; (3) the variables which must be controlled to change the system free energy are identified and displayed in a graph to illustrate their relationship; (4) and finally, X-heat experimental results, with corresponding system free energy expressed as D chemical potential, are superimposed on this graph.

The thermodynamic relationships developed here illustrate the need for a high operating temperature and a low system electron Fermi energy if commercial power densities are to be attained. Hopefully this insight will be useful in directing the next round of cold fusion research.

Introduction

The thermodynamic 'state' of a gas/solid system at equilibrium may be completely expressed in terms of three properly selected 'fundamental' variables.[Ref 2] In the case of the gas-loaded deuterium-palladium system, three such 'fundamental' variables are gas pressure, temperature, and concentration of the D solute. It is convenient to visualize the D-Pd system as having two sub-systems: (1) the solid Pd is the 'host' sub-system, and (2) the surrounding D_2 gas is the 'gas' sub-system. The dissolved deuterium becomes an interacting 'solute' in the host sub-system. The concentration of the deuterium solute in the host (D/Pd) is given, for any selected gas pressure and temperature, by the D-Pd TCP Equilibrium Diagram.(See Appendix I)

There are several sequential processes leading from an unloaded Pd host to the production of X-heat at a significant power density. They include (1) movement of the D+'s into the host and increasing the system free energy until some D+'s delocalize and assume the symmetry of the lattice and (2) achieving overlap of the D+ wave functions. These processes are shown

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[1] "X-Heat" is that heat generated as a result of a fusion reaction.

schematically in *Figure A*. (Chemical potential, μ, noted in *Figure A*, is discussed on the following page.)

Some of these processes are initiated and progress by intentional increases in the molal free energy of the gas sub-system which, in turn, causes corresponding increases in the system free energy associated with the dissolved deuterium in the bulk palladium host. These processes are the enabling processes that set the stage for the fusion reaction. The fusion reaction itself is spontaneous and results in a decrease in the system free energy which is the normal direction for a spontaneous reaction. Understanding the free energy changes therefore is very important to establishing the proper reaction controls.

Processes for Enabling a Fusion Reaction

The natural state of the 'free' electrons is the band state (bs). ('Bound' electrons are localized.)

Sum of 'free' electrons from all sources

$\mu_{e-_{max}} \approx \varepsilon F$

See Notes

Solution & diffusion
Dissociation

Some D+'s delocalize & daughter waves assume lattice symmetry when:

$\mu_{D+} \geq \mu_{D+crit}$

The reaction control is μ_{D+}

Gas T & P are the only controls to influence μ_{D+}

X-heat

Fusion occurs when coherent volume of crystals is $\geq 10^4$ cells & there is overlap

Notes:

1. μ_{D+} is the chemical potential of the D+ in the solid. (See text.)

2. μ_{e-max} is determined by the last electron to enter or leave an outer band. (Pauli exclusion principle)

3. The relationship between μ_{D+} and μ_{Dgas} is: $\mu_{D+} = \mu_{Dgas} - \varepsilon_F$ (See text)

   where: (a) $\mu_{Dgas} = 1/2\, RT \cdot Ln(P)$

   (b) ε_F is the electron Fermi energy.

4. μ_{D+crit} is a function of the Pd crystal characteristics.

Figure A

Gibbs Free-Energy and Chemical Potential

Gibbs free energy, F, is useful in determining what reactions are possible, what their direction is, and the conditions for equilibrium. For the D-Pd system, Gibbs free energy may be expressed in terms of the three fundamental variables, temperature, pressure and concentration. Experimental data on this relationship has existed for many years and is consolidated in Appendix I. This function, F, for a system which does work only against pressure, is defined as:[Ref 3]

$$F \equiv E + PV - TS \qquad \dots\dots\dots (a)$$

where E is the system internal energy, P is the pressure, V is the volume, T is the temperature and S is the entropy.

Differentiating equation (a), and combining it with statements of the first two laws of thermodynamics produces the very useful equation: [Ref 4]

$$dF = VdP - SdT \qquad \dots\dots\dots (b)$$

A useful function of the F is a sub-system property called 'chemical potential' with the symbol 'μ'. Chemical potential of a dissolved species is defined as the change in Gibbs Free Energy when one additional mol of the species is added to a large sub-system while holding the temperature, pressure and the concentration of other species constant. It may be viewed as the energy that would be required to force one more mol of a species into the system at its present thermodynamic state. In this paper, the chemical potential function, μ, will be used in two forms. One form is used for the pure D2 gas sub-system surrounding the host, and the other form is used for the D solute within the host palladium sub-system as just described. The next two sections derive the two forms.

In general, a process in a system is possible, and will occur spontaneously, if the process decreases the system Gibbs free energy, F. As an example, in the host sub-system, the deuterium entities, or *solute*, will move within the palladium bulk from a region of high chemical potential to one of low chemical potential. Equality of the entities' chemical potential throughout the system occurs at equilibrium[2] where its concentration within the bulk is essentially uniform. The uniform chemical potential of the solute achieved will be a function of the gas chemical potential established at the surface of the palladium host metal where the two sub-systems interface.

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[2] Consider that, as the process occurs, a certain variable decreases progressively and this variable is plotted against Gibbs free energy. The process will continue until a minimum is achieved on the 'F/variable' curve. This is the equilibrium condition.

## Chemical potential for the deuterium gas sub-system

For the homogenius deuterium gas sub-system, the D chemical potential is the *molal free energy*, F/n. [3] It is derived from equation (b) for a system at constant temperature (dT = 0), by replacing the V term with its equivalent in the ideal gas equation[4] and integrating between the limits of P and Po:

$$F/n = \mu_{Dgas} - \mu_{Dgas\,0} = 1/2\ RT \cdot Log_{natural}(P/P_0) \qquad \ldots\ldots\ldots (c)\ [5]$$

where: a mol, n, is taken as one D atom to be consistent with the D entities in the bulk of the palladium host;[6] R is the gas constant (8.32 J/mol°K); T is the temperature (K); P is the gas pressure (atm); and Po is a selected standard state pressure, taken here as 1 atm. When P=Po, $\mu_{Dgas} = 0$; therefore it is common practice to abbreviate the equation to read:

$$\mu_{Dgas} = 1/2\ RT \cdot Ln(P) \qquad \ldots\ldots\ldots (d)\ [7]$$

Figure B is presented to visualize how the gas chemical potential, μ_{Dgas}, is affected by the gas pressure and temperature. It is important to note that enormous pressures are required at room temperature to achieve even modest chemical potentials. On the contrary, at higher temperatures, much higher chemical potentials can be achieved at quite modest pressures.

Figure B

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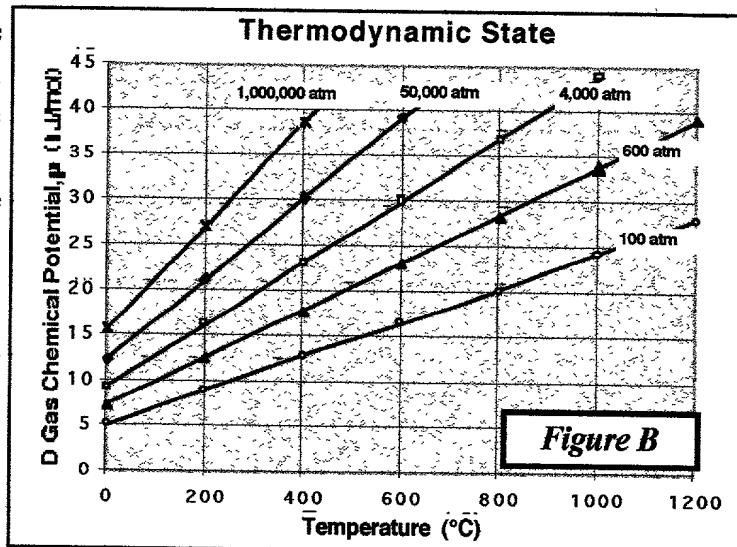
[3] See Ref 3, Lewis & Randall, p 148.

[4] A reminder that: (1) the Ideal Gas Equation is: PV=nRT and (2) that dP/P =Log_nP.

[5] See Ref 4, Darken & Gurry, equation 9=1.

[6] A mol of D2 gas produces 2 mols of D in the bulk Pd. Each such mol of D therefore has 1/2 of the free energy of the D2 mol.

[7] In common with all log functions, the logP functions cannot be used at P values near zero. At zero P, the log will equal minus infinity. It is best therefore to avoid use of very low pressures in calculations by comparing a given pressure with a standard-state of a finite positive value, using a subscript '0' to denote the selected standard state. In all of this work, a standard state pressure of 1 atmosphere is used along with actual pressures in atmospheres. Since log 1 is zero, the log of the pressure at the standard state is zero. The value of the pressure in equation (c) may therefore be correctly shown without the Po. It is important to always state the pressure units and the standard state. If one uses other units or another standard state, the chemical potential for a given system will be different and a correction must be made.

Chemical potential for the deuterium dissolved in the bulk palladium

The other form of chemical potential is for use with a host having dissolved mobile constituents. In this case, when a D entity moves from the *gas* sub-system to the *host* sub-system, it splits into a band state electron, e-, and a D+ ion which now become *two* species in the host. Also, a large interaction between the D+ and the host may be expected since work is performed on the Pd lattice to accomodate the new entities. Therefore, for the host sub-system, the total free energy is not the sum of the free energies of the solute and the host because of the interaction between them. Instead, it is necessary to determine the change in the system free energy due to a small addition of D, under conditions where the system temperature, pressure and the concentration of other species remain constant. [8]

In the general case, the chemical potential of species '1' is $\mu_1 \equiv (\partial F/\partial n_1)_{P,T,n2,n3...}$ where 'n' is the number of mols of each species.

The differential equation for the presence of two mobile species is:

$$dF = VdP - SdT \mp \mu_1 dn_1 \mp \mu_2 dn_2 \qquad ....(e) \text{ Ref 3}$$

Here the μ's are the chemical potentials of the solutes and indicate their *partial molal free energy*.

Total system free energy changes

To determine the effect on the D-Pd system when dn mols of D are transferred from the gas to the solute, the change in the total system free energy is expressed as follows:

$$dF = -\mu^-_{Dgas} + \mu_{e-} + \mu^-_{D+} \qquad ....(g)$$

At equilibrium, dF = 0, and

$$\mu_{Dgas} = \mu_{e-} + \mu_{D+} \qquad ....(h)$$

When considering the chemical potential of the electrons entering the system, it must be remembered that the 'free' electrons from the palladium host sub-system exist as delocalized

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[8] Note that the entrance of the D+ and e- entities into the host is accompanied by several types of heat and work with the net effect being a change the the system free energy. These transient effects include dissociation, ionization, heat of solution and lattice phase transformation. These heats are intentionally excluded from any long term X-heat effects.

'band state' electrons[9] where each occupies a 'permissible' energy state, one electron per energy state and spin, with the maximum state being the electron Fermi energy, ε_F. Any newly arrived electron can only enter an unoccupied energy state near ε_F which raises its maximum band state energy. The chemical potential of the 'last' electron to enter at equilibrium is approximately equal to the electron Fermi energy: [Ref7]

$$\mu_{e\text{-}max} \approx \varepsilon_F. \qquad \ldots\ldots\ldots (i)$$

Since our primary interest is in the thermodynamic state of the D+ solute, equation (h) may now be written to express the relationship between the *D solute* chemical potential and the *D gas* chemical potential as follows:

$$\mu_{D+} = \mu_{Dgas} - \varepsilon_F \qquad \ldots\ldots\ldots (j).$$

Reaction Control Parameters

Referring again to *Figure A*, to enable the fusion reaction, the chemical potential of the dissolved deuterium, μ_{D+}, must be increased to a 'critical' level[10] where some of the D+'s begin to delocalize forming daughter waves that assume the symmetry of the Pd lattice. When the palladium crystal characteristics are appropriate and there is overlap of the D daughter waves, the fusion reaction will occur.[Ref1] To accelerate the reaction rate, one must increase μ_{D+} above the critical level, μ_{D+crit}, thereby increasing the concentration of D daughter waves and overlap.[Ref6] There are, however, no direct controls for increasing the μ_{D+}. It is apparent that the intentional increase in the molal free energy of the gas sub-system is the primary method by which μ_{D+} is influenced. When equation (d) is incorporated into (j),

$$\mu_{\bar{D}+} = [\ 1/2\ RT \cdot Ln(P)\ ] - \varepsilon_{\bar{F}} \qquad \ldots\ldots\ldots (k)$$

it now becomes clear that not only must the *temperature*, **T**, and the *gas pressure*, **P**, of the gas sub-system be controlled, but the *electron Fermi energy*, ε_F must be kept to a minimum if significant reaction rates are to be achieved using achievable gas chemical potentials.[11]

Since the electron Fermi energy level is set by the 'last' electron to enter or leave the sea of band state electrons (as noted in the previous section), minimizing the number of 'free', or band state, electrons in the system is essential. Such things as removal of contaminants that may ionize and

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[9] When the palladium's free electrons delocalize, they form daughter waves that assume the symmetry of the crystal lattice. The 'bound' electrons remain localized.

[10] $\mu_{D+\ crit}$ is believed to be a function of the Pd crystal characteristics and the purity of the system.

[11] Achievable gas chemical potentials are limited by the reactor pressure vessel material strength at high temperatures.

removal of other metals that may contribute 'free' electrons are obvious actions that will help.

An obvious and large source of 'free' electrons is the deuterium solute itself. The energy relationship expressed in equation (k) strongly suggests that increasing the reaction temperature to raise the free energy of the gas sub=system will have two beneficial effects: (1) the gas pressures required to achieve high gas chemical potentials are significantly lower than otherwise and (2) the concentration of deuterium in the palladium, D/Pd, is reduced due to decreased solubility at high temperatures(Appendix I) with a commensurate reduction in the electron Fermi energy.

It has been common practice to strive for high D concentrations, while only incidentally achieving a high chemical potential. It now seems clear that high chemical potentials and *low* D concentrations are preferable. A high concentration of localized D+'s is irrelevant since the true reactants are the *delocalized* D+'s. *The formation of delocalized D+'s is dependent on the thermodynamic state of the D⊤'s, not their concentration, per se.*[12]

Figure C is presented to place the relationship in equation (k) in perspective. Here, two different sets of operating conditions which produce the same gas chemical potential are noted. A lower D/Pd at the higher temperature will reduce the electron Fermi energy and increase the chemical potential of the dissolved deuterium. Referring to the D-Pd Equilibrium Diagram, the D/Pd for the 300°C operating point is about 0.7 and for the 750°C point, D/Pd is less than 0.1. Please note that the finite

Thermodynamic State
Effects of the Electron Fermi Energy

Figure C

[A] Improvement due to higher temp.
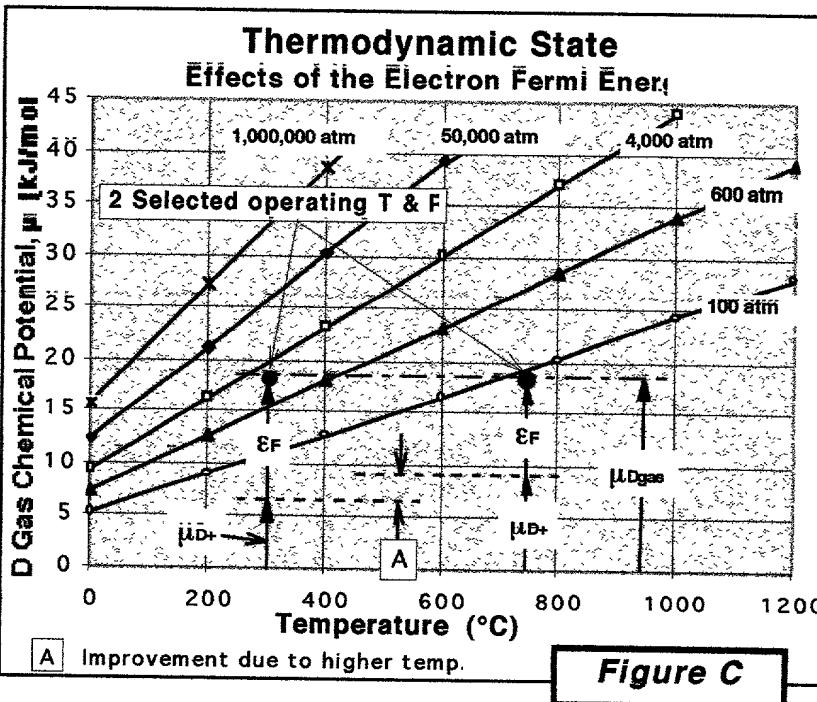
values of μ_{D+} and $\mathcal{E}_F$ are not known to these authors at this time; the presentation is intended only to indicate the trends.

Other potential benefits of high temperature are associated with restoring and maintaining the

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[12] The preference for high μ's and *low* D+ concentrations to achieve high power densities is consistent with the evidence produced by Fleischmann & Pons in their 'boil-to-dry' experiments.

appropriate crystal characteristics: (1) more rapid and complete healing of dislocations formed during D loading; (2) vaporization of some residual contaminants; (3) restoration of some deformed lattices and vacancies; etc.

Where does experimental data fit into this picture?

X-heat experimental results, with corresponding system free energy expressed as D chemical potential, are superimposed on the 'μ-T' graph in *Figure D* for comparison. Successful experiments are shown as solid bars. In phantom, some very high pressure (but unsuccessful) experiments are also noted which represent the highest known chemical potentials reached by gas loading. Note that when chemical potentials of 15 or 16 kJ/mol are achieved by electrolysis, the gas pressure in the voids in the palladium reaches as much as 200,000 atmospheres which severely damages the surrounding lattice structure and, no doubt, partly accounts for non-reproducibility.

Thermodynamic State
&
Chemical Potentials Achieved in Experiments

Figure D
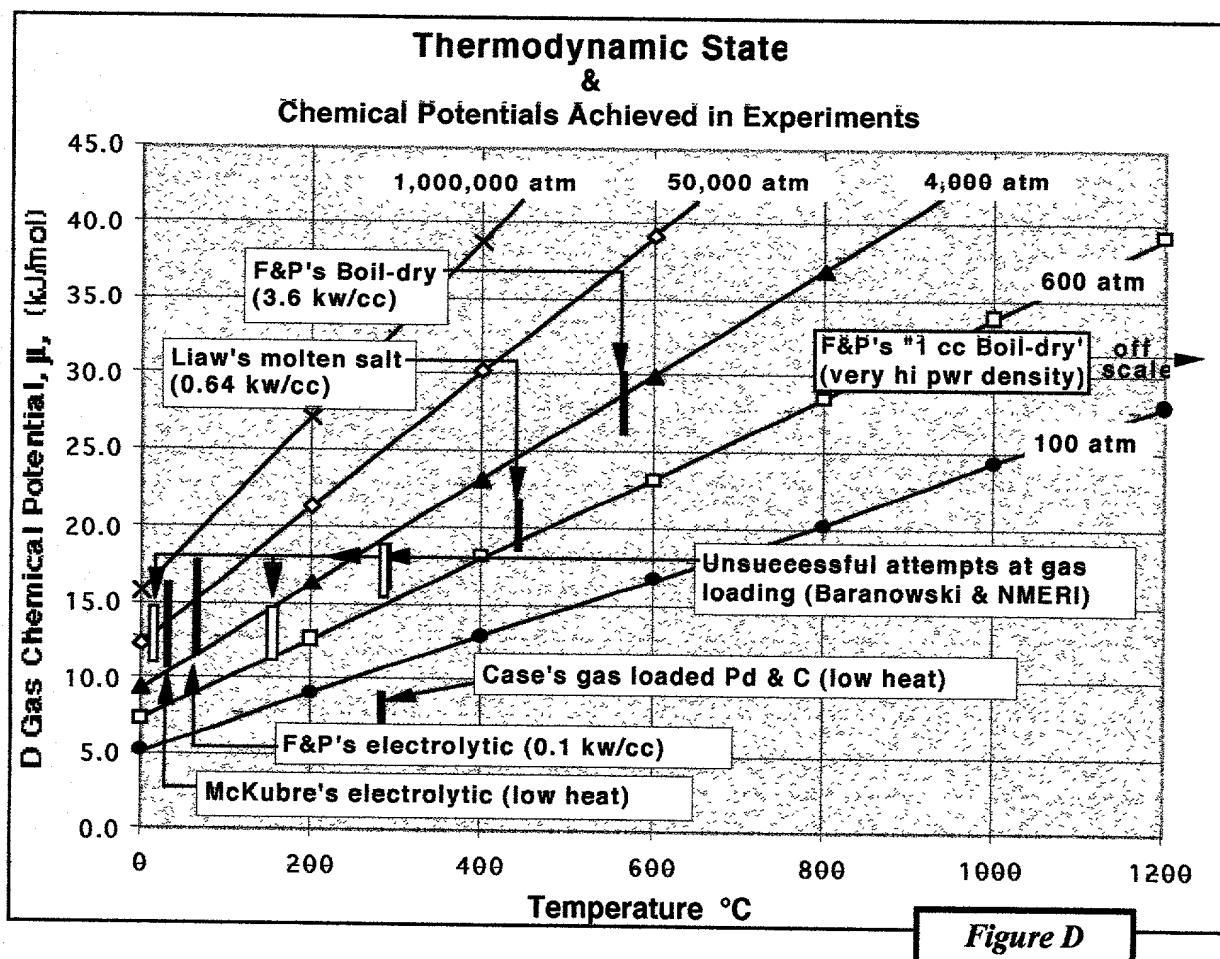
Note the reference to the 'off scale' results of the Fleishmann & Pons "*One Cubic Centimeter*" boil dry experiment[Ref 5] where a cube of solid palladium was being electrolized and accidentally

boiled off the electrolyte while unattended. Heat transfer was inadequate without the electrolyte and positive temperature feedback drove the sample to a very high temperature and sustained the reaction near its melting point of about 1550°C. The reacting sample 'burned' through the lab table and the floor in the process indicating a very high power density.

One can speculate that the effect was more than just the expected positive temperature feedback (following an exponential function of the temperature similar to a Boltzmann distribution). It seems likely that the electron Fermi energy was decreasing as well, due to lower D concentrations as temperatures climbed, permitting the small remaining dissolved D to reach very high chemical potentials. This synergistic effect could account for the very large power density that obviously was produced.

Summary

(1) The fusion reaction is enabled by raising the chemical potential of the dissolved deuterium, μ_{D+}, above its critical level by intentionally increasing the chemical potential of the surrounding deuterium gas, μ_{Dgas}. (See *Figure A* again)

(2) The equation governing the relationship between μ_{D+}^- and μ_{Dgas}^- is:

$$\mu_{D+} = [\ 1/2\ RT \cdot Ln(P)\ ] - \varepsilon_F\ ,$$ where T is the temperature in K, P is the gas pressure in atm, and ε_F is the electron Fermi energy and where each expression is in Joules/mol.

(3) To keep the threshold gas chemical potential requirements within reasonable limits, the electron Fermi energy should be minimized:
  (a) Operate at high temperatures and low D concentrations
  (b) Eliminate contamination that adds 'free' electrons to the system
  (c) Consider the possibility of alternative methods of removing 'free' electrons from the system while maintaining the essential characteristics of the Pd crystals.

Acknowledgments

Authors' Commentary

While providing high temperatures is one way of reducing the electron Fermi energy in the system, one can speculate that other methods may be found effective to accomplish the same thing. The addition of 'activated' materials, or 'catalysts', that have the ability to readily incorporate free electrons and become inert without changing the necessary palladium crystal characteristics is one such general area that may hold promise.

It seems to these authors, however, that the 'high temperature' approach has a high probability of success. It is likely that high temperatures will be required, in any event, to achieve power densities in the commercial range, therefore it would be an added benefit to gain experience in high temperature work now for later use in power reactor designs.

References

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Ref 2   Herbert B. Callen, "Thermodynamics and an Introduction to Thermostatistics", John Wiley and Sons, New York, 1985, p. 28.

Ref 3   Gilbert Newton Lewis & Merle Randall, revised by Kenneth Pitzer & Leo Brewer, "Thermodynamics", McGraw-Hill, 1961, Equation 10-10.

Ref 4 Lawrence S. Darkin & Robert W. Gurry, "Physical Chemistry of Metals", McGraw=Hill, 1953, p. 186.

Ref 5   M. Fleischmann, S. Pons & M. Hawkins, "Electrochemically Induced Nuclear Fusion of Deuterium", Journal of Elecrtoanalytical Chemistry 261 (1989) 301. See erratum, 263 (1989) 187.

Ref 6   TN=3.0 "Predicting the Power Production Rates for D=Pd Fusion Reactors" by J. L. Waisman & R. H. Summerl

Ref 7 Daniel D. Pollock, "Physical Properties of Materials for Engineers", Vol. I, CRC Press, Inc., Boca Raton, Florida, 1982, p 137.

The D-Pd TCP Equilibrium Diagram

Deuterium Gas Pressure - Atmospheres (y-axis)

Concentration - D/Pd Atomic Ratio (x-axis)
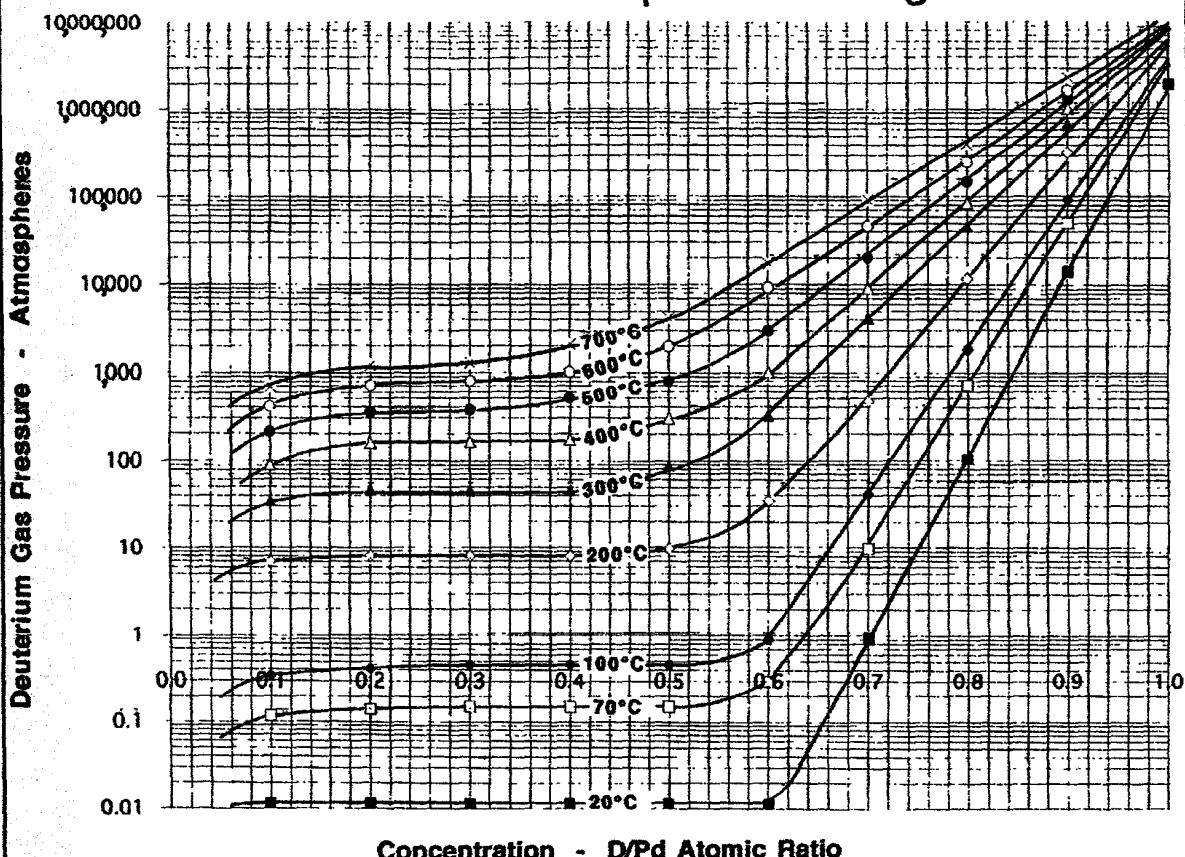
Notes

(1) This Equilibrium Diagram* of TCP isotherms is a composite of five sources of hydrogen TCP data and two sources of deuterium TCP data replotted on a single format. The hydrogen data has been adjusted by an experimentally determined factor to make it consistent with the deuterium data. The curves were smoothed, interpolated and extrapolated (above 1000 atm & 500°C) where necessary to complete the map. In reality, few points are 'true' lab data points. (See TN-1.0 "The TCP Equilibrium Diagram for the D-Pd System".)

(2) The values are taken to be an average for solid forms of palladium. For palladium black, the curves must be shifted about 0.02 to the right on the concentration scale.

(3) Every point on this map represents a condition of equilibrium where the D2 gas and the Pd body coexist. At equilibrium, the chemical potential of the deuterium is the same throughout the metal body and is a function of the chemical potential of the D2 gas at the surface of the metal.

(4) Every point represents the maximum average D concentration at a given T & P.

(5) If any two variables in a deuterium-palladium system are known, then the third variable is dependent and can be found on the Map.

*What is called the 'Equilibrium Diagram' here is sometimes referred to as: a 'TCP Diagram', a 'Phase Diagram', 'TCP Isotherms' or a 'TCP map'.
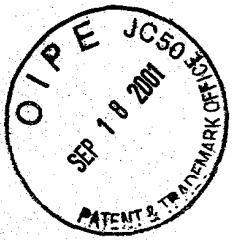
ICCF-8

Technical Paper

by

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[Replication of Experiments Measuring Helium & Tritium]

The Emergence of a Coherent Explanation for Anomalies Observed in D/Pd and H/Pd Systems: *Evidence for ^{4}He and ^{3}H Production*

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Introduction

Numerous observations have been made of apparent anomalies in carefully performed experimental studies of D/Pd and H/Pd systems. Such anomalies include: prompt emission of electrons and charged particles; unexplained heat in excess of known input sources; the residual presence of light elements (notably ^{3}H, ^{3}He and ^{4}He); the possible occurrence of isotope anomalies in higher mass elements (including the host metal); unusual electrical conductance effects both stable and transient (not discussed in this paper). The features that unify these apparently disparate observations are the common elements of the needed experimental stimuli, and the requirement for extended lattice coherent processes in any obvious explanation.

Presented in this paper are the results of four experiments conducted using palladium structures loaded with hydrogen or deuterium by gas and electrolytic means. The purpose was to evaluate possible evidence for d-d fusion reactions in lattice structures, in the temperature range 25-250°C. Primary evidence sought and evaluated were the appearance of anomalous excess heat accompanied by the production of light isotopes: ^{3}He and ^{4}He.

Description

Experiments were performed in four basic geometries:

1) Open cell electrolysis of D_2O at Pd and Pd-alloy wire cathodes using an accurate integral boundary Seebeck calorimetry.[1] These experiments were designed to replicate earlier observations of Miles et. al.[2] of the correlated appearance of excess heat and helium in glass cells. The experiments at SRI were performed in rigorously metal sealed cells incorporating active exclusion of ^{4}He to increase the measurement sensitivity and accuracy.

2) Loading of D_2 and H_2 into Pd on carbon supported catalyst using modest gas pressures (1-3 Atm.) and temperatures (170°–250°C). These experiments were designed to test the claim by Case[3] to observe excess temperature and increasing ^{4}He levels under similar conditions. Experiments at SRI were performed in sealed Nupro® 50 cc stainless steel vessels connected to a steel manifold. Periodic measurements of ^{4}He were made by direct connection to an Extrel® mass spectrometer capable of resolving the mass-4 peaks of D_2 and ^{4}He. Using information recorded from temperature sensors placed inside and outside active and reference gas cells it was possible to obtain heat-flow calorimetric information at times when the catalyst bed temperature rise was significant.

3) Closed cell electrolytic loading of D into Pd wire cathodes in a rigorously metal-sealed apparatus using highly accurate mass flow calorimetry.[1] These

experiments were intended to replicate earlier results of excess heat measurement at SRI in thermodynamically closed electrolytic loading cells, for which ambient exclusion of ^{4}He was not possible.[4,5]

4) Closed cell electrolytic loading of D (and H) into hollow Pd cathodes sealed to contain small dimension Pd-black powders. These experiments were performed to replicate published results by Arata and Zhang in which excess heat, ^{4}He and ^{3}He, were found to be associated with the electrolysis of such "double structured" cathodes[6] in D_2O, but not in H_2O. In experiments performed at SRI accurate mass flow calorimetry[4] was used to evaluate and compare the heat production of double structured cathodes electrolyzed in D_2O and H_2O in otherwise identical cells. The contents of the cathode void volumes were subjected to retrospective analysis for light isotopes.

Results

Figure 1 presents the results of concurrent excess power and helium measurements performed during open cell electrolysis using two different Pd and Pd-alloy cathodes. In three instances where excess power was measured at statistically significant levels, ^{4}He also was found to be conveyed out of the cell in the electrolysis gases ($D_2 + O_2$). The solid line in Figure 1 plots the regression fit of these data to a line passing through the origin; the dashed line is that expected for ^{4}He generation according to the reaction;
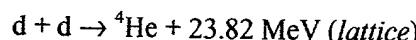
$$d + d \rightarrow \ ^4He + 23.82 \ MeV \ (lattice) \qquad [1]$$
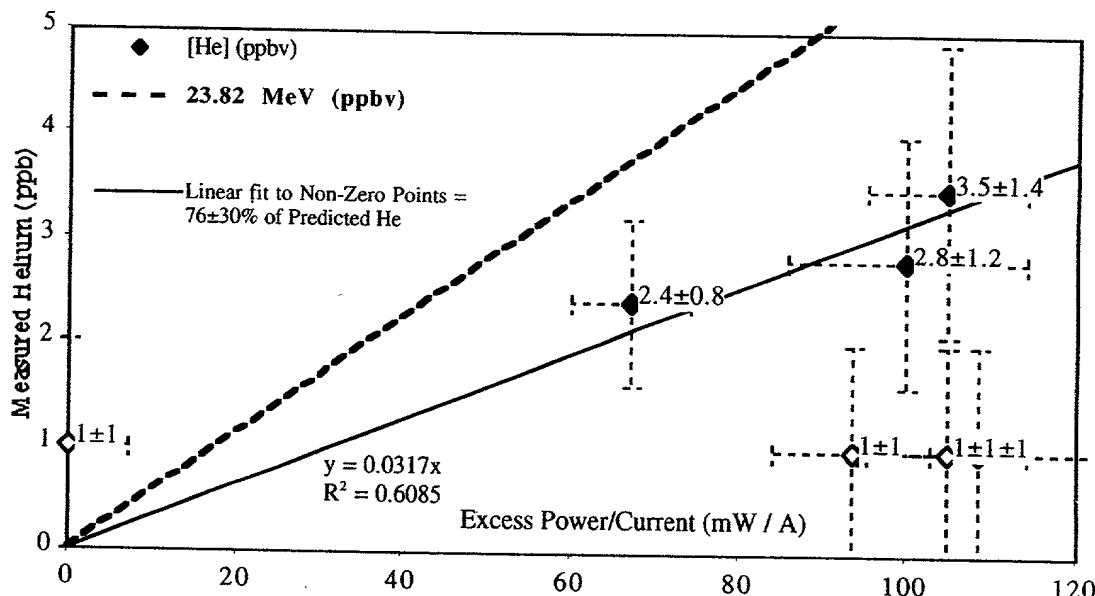
Figure 1   Correlation between rates of Heat and ^{4}He production in Seebeck Calorimeter.

It is clear from the slopes of these two lines that the observed [4]He constitutes only $76 \pm 30\%$ of the [4]He predicted by equation [1]. A more significant problem in Figure 1 is that three further [4]He samples, taken at times of non-zero excess power (open diamonds), exhibited helium concentrations only at the level of the analytical uncertainty, as did numerous samples taken in the apparent absence of excess power production. Clearly if [4]He is produced in association with excess power, it is not released to the gas phase immediately, or completely.

Experiments in category "2" in which Pd on C catalyst materials were exposed to D_2 and H_2 gases for prolonged periods, exhibited a range of behaviors. Figure 2 summarizes 6 of 16 results obtained in paired cells.
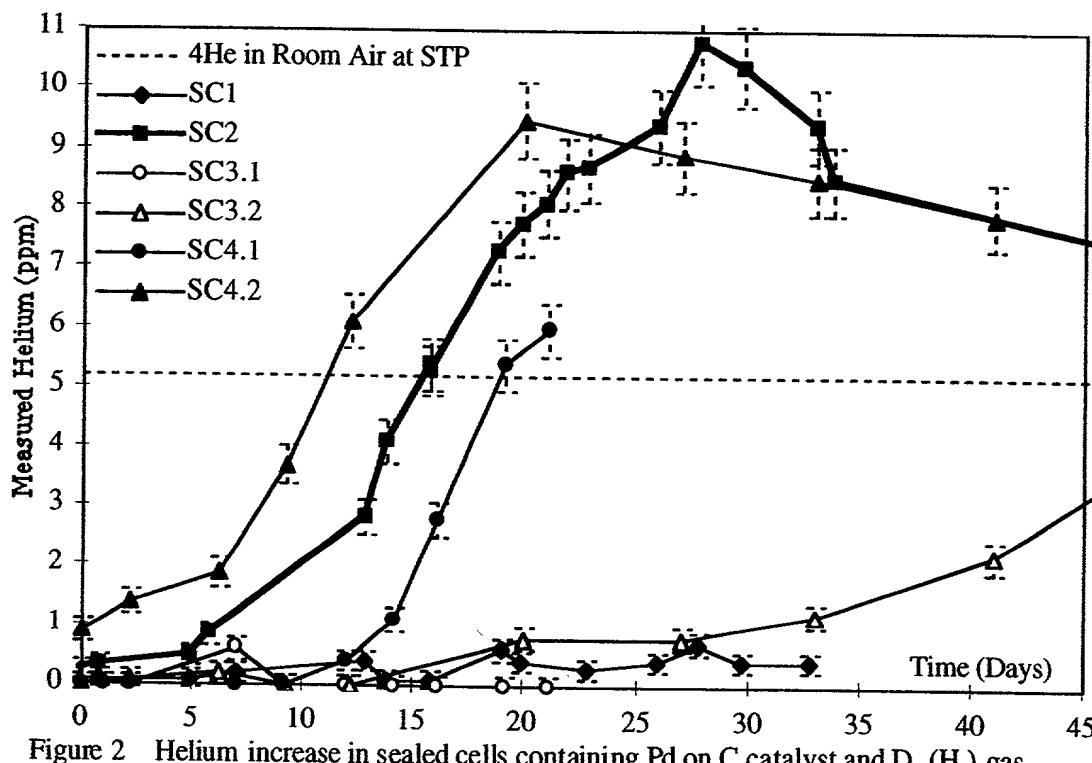
Figure 2   Helium increase in sealed cells containing Pd on C catalyst and D_2 (H_2) gas.

Using direct, on-line, high-resolution mass spectrometric measurement of [[4]He] we observed the following behaviors:

(i)   cells that show no increase of [4]He over long periods of time (including all cells operated with H_2 instead of D_2);

(ii)   cells that exhibit a slow, approximately exponential increase in [[4]He] with time;

(iii) cells that display no measurable increase in [[4]He] for a period of several days, followed by a rapid, approximately linear rise in [[4]He] to levels sometimes exceeding that of the ambient background.

Using data from temperature sensors placed in the catalyst and gas phases, and situated in the room, we are able to make heat flow estimates in one of two ways:

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a) a <u>Gradient</u> method, based on the relationship between the temperature difference between catalyst bed and confined gas, and the heater input power;
b) a <u>Differential</u> method, based on the temperature differences between active and reference catalyst bed sensors, and room temperature, as a function of the relative input heater powers.

The energy estimated in excess of that provided by the heater for these two calorimetric methods is plotted in Figure 3, together with the measured helium concentration during the time of greatest derivative, $\partial[^4He]/\partial t$ in experiment SC2. It is clear that the appearance of excess heat and the apparent increase in [^{4}He] are temporally correlated.
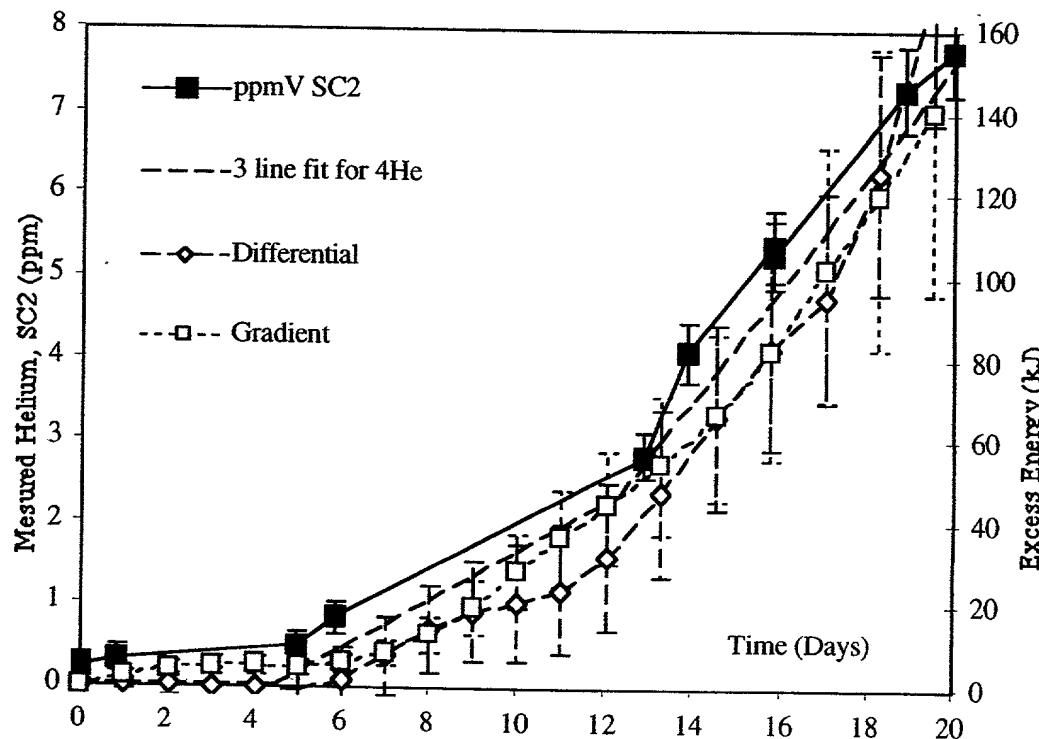
Figure 3   Correlation of Heat and Helium Production in D2 Gas Cell.

In an attempt to establish a quantitative correlation, Figure 4 plots the two calorimetric estimates of excess heat production interpolated from Figure 3, versus the measured increase in [^{4}He] (the value plotted in Figure 3 minus the ^{4}He initially present in the D_2 gas). Regression lines through these data incorporating the origin have slopes: Q=31 ± 13 and 32 ± 13 MeV per ^{4}He atom, respectively, for the gradient and differential calorimetric methods. Although these Q values include that of reaction [1] within their assigned uncertainties, the mean values for the ^{4}He presented directly to the gas phase for analysis is only ~75% of that predicted by equation [1].
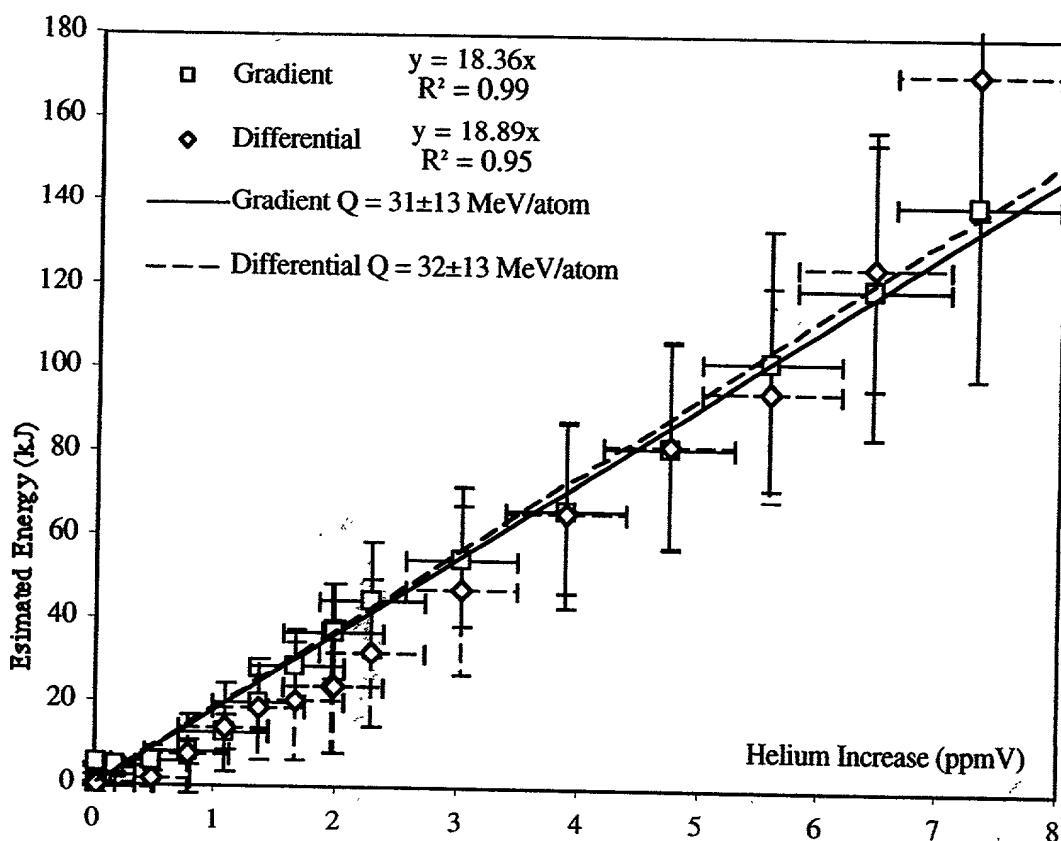
Figure 4 Estimated Energy versus Helium Increase.

Clarification of a possible origin for the apparent ^{4}He deficit in experiments "1" and "2" can be obtained from the results of experiment "3". Approximately 82 kJ of excess heat was measured in the electrolysis of a 100 mm x 1mm Pd wire cathode in D_2O. This experiment was performed in a rigorously metal sealed and helium leak-tested cell and apparatus provided with the facility to sample the gas in the headspace. When initially analyzed following a period of excess power production, the gas phase contained only 62% of the ^{4}He expected if reaction [1] were the source of the excess heat. A second sample showed an increase in [^{4}He] despite the fact that the helium content of the vessel had been diluted with D_2 containing low levels of ^{4}He, in order to make up the initial gas volume after the first gas sample. Taking these increases as evidence of sequestered ^{4}He, the cathode was subjected to an extended period (~200 hours) of compositional and temperature cycling by varying the current density in both anodic and cathodic directions.

A mass balance of ^{4}He was calculated based on two further gas samples: one to determine the helium content of the D_2 gas used initially to fill and refill the sealed metal cell (0.34 ± 0.007 ppmV); the other to measure the final helium concentration in the gas phase after exercising the cathode to release trapped gases (2.08 ± 0.01 ppmV). Taking into account the amounts lost by sampling, and introduced with make-up D_2, a calculated mass balance for ^{4}He in the gas phase after compositional and thermal cycling of the

cathode results in a number that is 104 ± 10% of the number of atoms quantitatively correlated with the observed heat via reaction [1].

The results of experiment "4" generally confirm those published earlier by Arata and Zhang of the appearance of excess heat in the electrolysis of "double structured" palladium cathodes[6] in D_2O, but not in H_2O. Figure 5 plots the calorimetric results of cathodically exercising two nominally identical cathodes in intentionally similar cells, one in 0.1M LiOD and the other in 0.1 M LiOH. In the same range of input powers, the heavy water cells yields clearly more output heat (plotted as excess power) than does the light water cell.
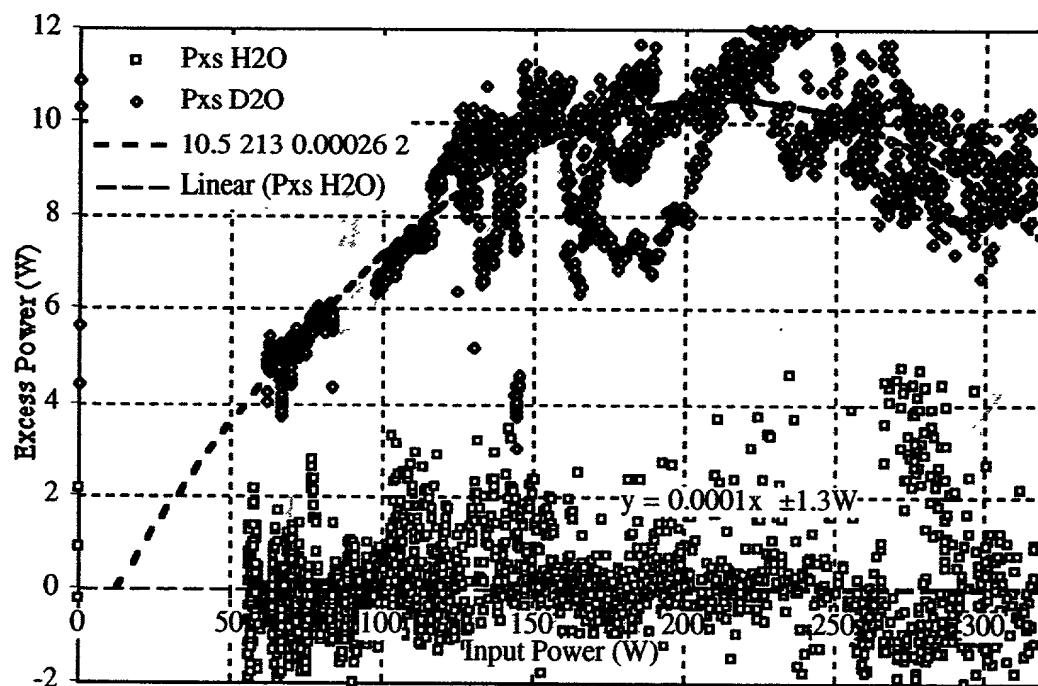
Figure 5   Excess Power versus Input Power measured for Arata-Zhang Double
Structured Cathodes using Mass Flow Calorimetry.

The maximum excess power observed in D_2O was 9.9 ± 1.3% of the measured power input, with the average value being approximately half the maximum. The measured power excess exceeded the experimental uncertainty (1-2%) for a period of ~86 days to produce an integrated energy excess of 64 ± 6 MJ for the D_2O cell. For the H_2O cell in the same period of time the measured energy excess was –1 ± 6 MJ.

At the conclusion of the experiment, both cathodes were removed and placed successively in a sealed chamber where they were punctured mechanically, and the gas contents of the cathode void volumes were extracted for analysis[7]. The Pd black powders also were removed and the Pd metal walls of the hollow cathodes were sectioned for analysis.

Significant amounts of tritium and ^{3}He from the decay of tritium were found inside the double structured volume of the cathode electrolyzed in heavy water. Small amounts of ^{4}He were attributed to atmospheric contamination. Detailed results are presented by Clarke et al[8].

Conclusions

There exists a strong time correlation between the rates of heat and helium production measured using on-line high-resolution mass spectrometry. In experiments performed using three different metal sealed cells, three different calorimetric methods, by electrochemical and gas loading means and with ^{4}He analyses made at three different institutional laboratories, there is observed a quantitative or near-quantitative correlation between heat and ^{4}He production consistent with the reaction:

$$d + d \rightarrow {}^4He + 24 \text{ MeV } (lattice)$$
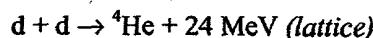
Evidence for near-surface retention of ^{4}He in the lattice can be used to accommodate the discrepancy between measured and expected yields of ^{4}He.

Evidence was obtained for excess heat production in the electrolysis of D_2O using "double structured" cathodes, supporting original claims by Arata and Zhang[6]. Associated with this result, although not quantitatively correlated to it, is the production of a significant amount of tritium and ^{3}He from the decay of tritium within the cathode void volume, suggesting the presence of a second nuclear reaction.

Acknowledgment

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